Highly Correlated Electron Materials: Dynamical Mean Field Theory

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One of the hallmarks of strongly correlated electron materials is their extreme sensitivity to small changes of parameters such as temperature, pressure, structural distortion, or impurity concentration [1]. This sensitivity is the result of a striking competition between kinetic energy associated with electron hopping in narrow bands and intra-atomic Coulomb repulsion. It gives rise to a fascinating range of electronic and magnetic phenomena whose understanding has been at the focus of fundamental research in condensed matter physics for many years. In addition, strongly correlated electron systems, in particular, transition metal oxides, are presently of great interest because of the possibility of utilizing them for technological applications.

An example which illustrates the range of phenomena that are observed due to small changes of external parameters is Ca$_{2-x}$Sr$_x$RuO$_4$. It has the same layer perovskite structure as the famous high-$T_c$ superconductors, with transition metal ions at the center of oxygen octahedra (see Fig. 1, left panel). Although the replacement of Sr via Ca is iso-electronic, the structural distortions caused by the smaller size of Ca indicated in the right panel give rise to a remarkably rich phase diagram (see Fig. 2, left panel): The pure Sr ruthenate ($x = 2$) is superconducting with $T_c = 1.5$ K, whereas the pure Ca compound ($x = 0$) is a paramagnetic or anti-ferromagnetic insulator. At finite $x < 0.5$, other magnetic phases are observed, while the range $x > 0.5$ is paramagnetic.

Density functional theory (DFT) in the local density approximation (LDA) predicts Ca$_2$RuO$_4$ to be metallic rather than insulating. This failure is quite typical for many transition metal oxides, including V$_2$O$_3$ and LaTiO$_3$. It is caused by the inadequate description of the Coulomb interaction within the partially filled $d$ electron shell. This interaction is comparable or larger than the hopping interaction between atoms and cannot be simply expressed in terms of the local
Fig. 2: Left: Iso-electronic phase diagram of Ca_{2-x}Sr_xRuO_4, with superconducting (SC) phase for $x = 2$, paramagnetic and canted anti-ferromagnetic insulating phases (PI and CAFI) for $x \rightarrow 0$ [2]. Right: wide $d_{xy}$ and narrow $d_{xz,yz}$ Ru $t_{2g}$ bands of Sr$_2$RuO$_4$ [3].

electron density. In some systems, the combination of LDA with an onsite Coulomb interaction – the so-called LDA+U method [4] – can explain the insulating behavior observed in long-range anti-ferromagnetic phases (see lectures by G. Bihlmayer). In general, however, the transition from metal to insulator requires a more refined formalism that accounts explicitly for quantum mechanical fluctuations within electron shells. The possibility of a purely correlation driven transition between paramagnetic metallic and insulating phases was first discussed by Mott about 60 years ago [5]. A theoretical formulation of such a transition in realistic materials, where metallic and insulating properties are treated on the same footing, can be achieved via the Dynamical Mean Field Theory (DMFT) [6, 7, 8] which is the subject of this lecture.

The unit cells of strongly correlated materials tend to have complex shapes, with several different types of atoms (see Fig. 1). An important first step towards a theoretical description is therefore the detailed one-electron calculation of the electronic properties within the LDA. There exist nowadays various codes which provide sophisticated information on many of these properties. Since many-body calculations become exponentially more time-consuming with increasing number of orbitals, the second step consists in identifying those partially filled bands near the Fermi level $E_F$ in which Coulomb interactions lead to the most dramatic effects. In the case of Sr$_2$RuO$_4$, these are the three Ru 4$d$ $t_{2g}$ bands where, because of the layer structure, $d_{xy}$ is a nearly two-dimensional wide band and $d_{xz,yz}$ are nearly one-dimensional narrow bands, all of which are about 2/3 filled (total filling is $n = 4$), see Fig. 2 right panel. Because of the octahedral crystal field, the $e_g$ bands ($d_{x^2-y^2}$ and $d_{z^2}$) are empty. Although the O 2$p$ bands are filled, it is important to keep in mind that hopping between Ru 4$d$ orbitals takes place indirectly via O ions which are located between Ru ions. Sr 5$s$ orbitals form empty bands far above $E_F$. The bands close to $E_F$ can therefore be described in terms of an effective single-particle Hamiltonian $H(k)$ (in the present case a $3 \times 3$ matrix) with band energies $\epsilon_m(k)$, where $m$ is the band index.

The main changes of the independent-particle band structure due to Coulomb interactions are shifts of band energies giving rise to band narrowing, life-time broadening, and new excited states (satellites or Hubbard bands) that do not occur within the single-electron picture. Thus,
correlations cause a transfer of spectral weight from low to high energies. Another important consequence of Coulomb interactions occurring in multi-band materials is that orbital occupancies of interacting bands can differ from those of non-interacting bands. As discussed in [9], in Sr$_2$RuO$_4$ this effect arises since the narrow $d_{xz,yz}$ subbands are more strongly correlated than the wide $d_{xy}$ band. Of course, the total number of electrons does not change due to Coulomb effects, but how these electrons are distributed over the various conduction bands depends on how they interact. Thus, Coulomb correlations can lead to inter-orbital charge transfer, i.e., to an increase or decrease of orbital polarization. In the following sections we discuss this kind of correlation induced internal charge transfer in a variety of transition metal oxides.

The phenomena discussed above can be theoretically formulated in terms of a complex self-energy $\Sigma(k, \omega)$. The Green’s function describing the electron motion through the crystal is

$$G(k, \omega) = \frac{1}{\omega + \mu - H(k) - \Sigma(k, \omega)},$$

where $\mu$ is the chemical potential insuring the correct total electron count. Neglecting matrix element effects associated with the frequency and polarization of the incoming light, the imaginary part of this Green’s function is proportional to the photoemission intensity for the point $k$ of the Brillouin Zone. For clarity we omit here orbital indices. Thus all quantities are assumed to be matrices in orbital space. The spin index is also dropped since we consider only paramagnetic systems. Because of the translational symmetry of the crystal, the lattice Fourier transform of $G$ is defined as

$$G_{ij}(\omega) = \sum_k e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \frac{1}{\omega + \mu - H(k) - \Sigma(k, \omega)},$$

so that the so-called ‘local’ Green’s function is given by the expression

$$G(\omega) \equiv G_{00}(\omega) = \sum_k \frac{1}{\omega + \mu - H(k) - \Sigma(k, \omega)}.$$  

Analogous equations can be written down for the self-energy. Since $H(k)$ is known, the main task is now to find some (approximate) scheme for the evaluation of $\Sigma(k, \omega)$.

## 2 Dynamical Mean Field Theory

The great appeal of DMFT is that it is applicable at weak and strong Coulomb interactions, and that it describes metallic and insulating behavior in a consistent manner. Let us consider the Hubbard model with on-site Coulomb interactions:

$$H = - \sum_{ijmn\sigma} t_{mnj}c_{im\sigma}^+c_{jn\sigma} + \sum_{im} U n_{im\uparrow}n_{im\downarrow} + \frac{1}{2} \sum_{im \neq \nu \sigma'} (U' - J\delta_{\sigma\sigma'}) n_{im\sigma}n_{im\sigma'},$$

$$- \sum_{im \neq \nu m'} J[c_{im\nu\uparrow}c_{im'\sigma\uparrow}^+c_{im'\sigma\downarrow} + c_{im\nu\downarrow}c_{im'\sigma\uparrow}^+c_{im'\sigma\downarrow}],$$

where $m, n$ are orbital indices, $i, j$ denote lattice sites $\mathbf{R}_{ij}$, and $t_{mnj}$ is the lattice Fourier transform of $H(k)_{mn}$. $U$ and $U'$ are intra- and inter-orbital Coulomb matrix elements and $J$ is the Hund exchange integral. Below we consider mainly systems involving $t_{2g}$ orbitals.
The key conceptual feature of DMFT is that, instead of solving the hopelessly complicated Hamiltonian defined above, a simpler version is considered where Coulomb interactions are retained only at one site (say at $i = 0$) while at all other sites they are replaced by the local self-energy. Thus the interacting lattice is approximated by a single interacting site which is surrounded by a lattice with an extra complex potential given by $\Sigma(\omega)$. The appropriate Green’s function $G'$ for this ‘impurity’ problem can be derived by using the Dyson equation which removes $\Sigma(\omega)$ from the origin. Thus,

$$G'_{ij}(\omega) = G_{ij}(\omega) - G_{i0}(\omega)\Sigma_{00}(\omega)G'_{0j}(\omega).$$ (5)

For the special case $i = j = 0$, and with the abbreviations $\Sigma(\omega) \equiv \Sigma_{00}(\omega)$, $G(\omega) \equiv G_{00}(\omega)$, and $G_0(\omega) \equiv G'_{00}(\omega)$, we find the important relationships

$$G_0(\omega) = [G^{-1}(\omega) + \Sigma(\omega)]^{-1},$$ (6)

$$\Sigma(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega).$$ (7)

The physical meaning of $G_0(\omega)$ is the following: It describes electronic motion from site $i = 0$ through the actual crystal and returning to $i = 0$, with one-electron hopping specified by the coefficients $t_{imjn}$. This motion, however, takes place within an extra complex potential given by $\Sigma(\omega)$ at all sites except $i = 0$.

Graphically we can represent the above approximation as follows:

```
U U U  Σ Σ Σ  Σ Σ Σ
U U U  Σ U Σ  Σ Σ Σ
U U U  Σ Σ Σ  Σ Σ Σ
```

The true interacting lattice on the left is simulated via the single-site interacting impurity at the center. The spectral information to be compared with photoemission data then follows from the lattice on the right, where all sites have a complex local self-energy. The picture at the center demonstrates the importance of removing the local self-energy from the origin before starting the many-body impurity calculation. If $G(\omega)$ were used in this step rather than $G_0(\omega)$, one would add the Coulomb terms involving $U$ to the local $\Sigma(\omega)$, which would amount to a severe double-counting of Coulomb interactions.

How do we find the so far unknown self-energy for the impurity calculation at the center? This is done iteratively, by starting with some reasonable guess, or by putting $\Sigma(\omega) = 0$. We then proceed via the following steps:

1. calculate $G(\omega)$ via Eq. (3)
2. calculate $G_0(\omega)$ via Eq. (6)
3. calculate new $G(\omega)$ via impurity solver (see below)
4. calculate new $\Sigma(\omega)$ via Eq. (7) and return to step 1.

Typically 10 to 20 iterations are required to achieve convergence, except close to metal insulator transitions where convergence tends to be slower.

For the quantum impurity calculation a variety of methods is available, such as quantum Monte Carlo (QMC), exact diagonalization (ED), numerical renormalization group (NRG), density
Fig. 3: Level scheme for exact diagonalization [11]. ε_{1,2,3} denote the t_{2g} orbitals at the impurity site which interact via Coulomb and exchange interactions. Each of these levels hybridizes with its own set of bath levels. Levels 2 and 3 and their baths are assumed to be degenerate.

matrix renormalization group (DMRG), iterated perturbation theory (IPT), non-crossing approximation (NCA), etc. The first two are the most accurate and versatile ones for realistic materials. They are complementary in the sense that their range of applicability and/or computational tractability differs somewhat. Where they overlap they have been shown to be in excellent numerical agreement. Here we focus on exact diagonalization [10] which during the recent years has been demonstrated to be a highly useful and efficient method for a variety of multi-band systems [11]. Compared to QMC it does not suffer from sign problems. Thus, it is applicable at rather low temperatures, large Coulomb energies, and for full Hund exchange.

In the procedure outlined above we have effectively replaced the true lattice self-energy Σ(k, ω) by its local version Σ(ω) which may be viewed as lowest order term in a lattice site expansion of Σ(k, ω). To go beyond this ‘single-site’ or ‘local’ approximation one needs to retain Coulomb interactions explicitly in a (small) cluster of sites rather than only at i = 0. Although the many-body problem then becomes computationally much more involved, there is currently considerable interest in cluster extensions of DMFT since the momentum dependence of the self-energy can have a significant influence on the nature of the metal insulator transition (see Section 10).

3 Multi-Band Exact Diagonalization

To solve the single-site quantum impurity problem within ED/DMFT, the true lattice environment of the impurity at i = 0 is simulated via a discrete set of non-interacting ‘bath’ levels. Thus, instead of H defined in Eq. (4) we consider the finite ‘cluster’ sketched in Fig. 3:

\[
H^{cl} = \sum_{mσ} ε_m n_{mσ} + \sum_{kσ} ε_k n_{kσ} + \sum_{mkσ} V_{mk} [c^+_{mσ} c_{kσ} + H.c.] + \sum_{m} U n_{m↑} n_{m↓} \\
+ \frac{1}{2} \sum_{m \neq m'} (U' - J δ_{σσ'}) n_{mσ} n_{m'σ'} - \sum_{m \neq m'} J [c^+_{m↑} c_{m↓} c^+_{m'↑} c_{m'↓} + c^+_{m↓} c_{m↑} c^+_{m'↓} c_{m'↑}].
\] (8)

The levels representing the impurity orbitals are ε_m, the levels of the surrounding bath are ε_k, and the V_{mk} specify the hybridization interactions between impurity and bath levels. The
remaining Coulomb and exchange interactions at the impurity site are identical to those of the original lattice Hamiltonian in Eq. (4). The site index \( i = 0 \) is dropped for convenience. The total number of cluster levels is denoted as \( n_s \). (The term ‘cluster’ refers here in ED to impurity + bath and should not be confused with cluster extensions of DMFT.)

The non-interacting cluster Green’s function is given by

\[
G_{0,m}^{\text{cl}}(i\omega_n) = (i\omega_n + \mu - H_{0,m}^{\text{cl}})^{-1},
\]

where \( H_{0,m}^{\text{cl}} \) represents the first three terms of \( H^{cl} \). Since we are interested in correlation effects at finite temperatures we evaluate Green’s functions and self-energies at Matsubara frequencies \( \omega_n = (2n + 1)\pi/\beta \), where \( n \geq 0 \) and \( \beta = 1/T \) [12]. If \( G_{0,m}^{\text{cl}} \) is diagonal in orbital space this expression can be easily reduced to

\[
G_{0,m}^{\text{cl}}(i\omega_n) = \frac{1}{i\omega_n + \mu - \varepsilon_m - \sum_k \frac{|V_{mk}|^2}{i\omega_n + \mu - \varepsilon_k}}^{-1}.
\]

The energy levels and hopping terms appearing in the cluster Hamiltonian Eq. (8) do not have any physical meaning. Their sole purpose is to achieve an accurate ‘cluster’ representation of the corresponding lattice impurity Green’s function \( G_{0,m}(i\omega_n) \). A standard conjugate gradient fitting routine can be used to find the cluster parameters, such that \( G_{0,m}(i\omega_n) \approx G_{0,m}^{\text{cl}}(i\omega_n) \), where we assume again diagonality in orbital space.

Once the non-interacting cluster parameters are found, the eigenvalues \( E_\nu \) and eigenstates \( |\nu\rangle \) of the many-body cluster Hamiltonian are evaluated via exact diagonalization. The finite temperature interacting cluster Green’s function is given by [12]

\[
G_m^{\text{cl}}(i\omega_n) = \frac{1}{Z} \sum_{\nu\mu} \frac{|\langle \nu | c^+_m \sigma | \mu \rangle|^2}{E_\nu - E_\mu + i\omega_n} e^{-\beta E_\nu + \beta E_\mu}.
\]

\[
= \frac{1}{Z} \sum_{\nu} e^{-\beta E_\nu} \left( \sum_{\mu} \frac{|\langle \nu | c^+_m \sigma | \mu \rangle|^2}{E_\nu - E_\mu + i\omega_n} + \sum_{\mu} \frac{|\langle \nu | c^+_m \sigma | \mu \rangle|^2}{E_\mu - E_\nu + i\omega_n} \right),
\]

where \( Z = \sum_{\nu} e^{-\beta E_\nu} \) is the partition function. Applying Eq. (7) to the cluster, we find

\[
\Sigma_m^{\text{cl}}(i\omega_n) = G_{0,m}^{\text{cl}}(i\omega_n)^{-1} - G_m^{\text{cl}}(i\omega_n)^{-1}.
\]

The key assumption is now that this ‘cluster’ self-energy is a physically reasonable representation of the lattice self-energy, \( \Sigma_m^{\text{cl}}(i\omega_n) \approx \Sigma_m(i\omega_n) \), which can then be inserted in \( G_m(i\omega_n) \). Evidently, at each iteration step two projections are carried out: (i) The lattice impurity Green’s function \( G_0 \) is projected onto the corresponding cluster Green’s function \( G_0^{\text{cl}} \); and (ii) the cluster self-energy \( \Sigma^{\text{cl}} \) is projected onto the lattice self-energy \( \Sigma \). In ED, each iteration therefore involves the following steps:

\[
\Sigma \rightarrow \textbf{G} \rightarrow G_0 \rightarrow G_0^{\text{cl}} \rightarrow \textbf{G}^{\text{cl}} \rightarrow \Sigma^{\text{cl}} \rightarrow \Sigma.
\]

To illustrate the quality of the projection \( G_0 \rightarrow G_0^{\text{cl}} \) we show in Fig. 4 Im \( G_{0,m}(i\omega_n) \) obtained from

\[
G_{0,m}(i\omega_n) = \int d\omega \rho_m(\omega)/(i\omega_n - \omega),
\]

which corresponds to Eq. (6) in the non-interacting limit \( \Sigma = 0 \) for diagonal \( G \). [Note that Im \( G_{0,m}(i\omega_n \rightarrow 0) \rightarrow -i\pi \rho_m(0) \) and Im \( G_{0,m}(i\omega_n \rightarrow \infty) \rightarrow 1/i\omega_n \).] As density of states
Fig. 4: Upper left: $a_g$ and $e'_g$ density of states components of V$_2$O$_3$ [13]; upper right: spectral distributions at real $\omega$ derived from Eq. (10) after fit along Matsubara axis. Bottom: comparison of Green’s functions at imaginary frequencies for two temperatures. Solid red curves: $\text{Im} \ G_{0,m}(i\omega_n)$, Eq. (14); blue dots: $\text{Im} \ G_{0,m}^{\text{cl}}(i\omega_n)$, Eq. (10).

For $\rho_m(\omega)$ we take the $a_g$ and $e'_g$ components corresponding to V$_2$O$_3$ [13] (see Section 7). These lattice impurity Green’s functions $G_{0,m}(i\omega_n)$ are compared with fits achieved via Eq. (10), where each impurity orbital is assumed to hybridize with three bath levels, as sketched in Fig. 3. At real frequencies $G_{0,m}$ has a continuous spectral distribution given by the density of states component $\rho_m(\omega)$, whereas $G_{0,m}^{\text{cl}}$ is discrete by construction (a small artificial broadening is included for illustrative purpose). Nevertheless, along the Matsubara axis both are seen to be in excellent agreement. This comparison demonstrates that, for finite clusters, the representation at Matsubara frequencies is not unique. In fact, within a certain accuracy, $G_{0,m}(i\omega_n)$ derived from a continuous real-$\omega$ spectrum can be represented via an infinite number of discrete spectra corresponding to different cluster sizes $n_s$. Because of the projections $\text{lattice} \rightarrow \text{impurity} \rightarrow \text{lattice}$ indicated in Eq. 13, continuous lattice and discrete cluster versions of Green’s function and self-energies are assumed to exist at each iteration of the ED/DMFT procedure (see also Sections 4 and 8).

Because of the Boltzmann factor in Eq. (11), at low $T$ only a small number of eigenstates of $H^{\text{cl}}$ are needed. Moreover, $H^{\text{cl}}$ is block-diagonal in spin sectors, consisting of extremely sparse submatrices. The eigenstates can therefore be efficiently evaluated by using the Arnoldi algorithm [14]. Basis vectors are of the form $|n_{\uparrow}, \ldots, n_{n_s\uparrow}, n_{\downarrow}, \ldots, n_{n_s\downarrow}\rangle$, where $n_{\sigma} = 0$ or 1. For $n_s = 12$, the largest spin sector corresponds to $n_{\uparrow} = n_{\downarrow} = 6$, yielding matrix dimension $N = d(n_{\uparrow}) \times d(n_{\downarrow}) = 924^2 = 853776$, where $d(n_{\sigma}) = n_{\sigma}!/[n_{\sigma}!(n_{\sigma} - n_{\sigma})!]$. The sums over
Fig. 5: Left: Comparison of Sr$_2$RuO$_4$ quasi-particle spectra derived using QMC/DMFT with tight-binding density of states. Solid (dashed) curves: $d_{xy}$ ($d_{xz,yz}$) distributions. Right: comparison of quasi-particle band structure with tight-binding bands (symbols) [9].

$\mu$ in Eq. (11) can be readily obtained via a Lanczos procedure after applying $c_{m\sigma}$ and $c_{m\sigma}^+$ to the excited states $|\nu\rangle$. Most of the examples discussed in the subsequent sections are for $t_{2g}$ bands, where each orbital couples to only two bath levels, giving $n_s = 9$ with $N = 126^2$. Since the baths of the impurity levels interact indirectly via the on-site Coulomb interaction, the level spacing of excited states is very small. Thus, convergence with cluster size is achieved far more quickly than in the single-band case which requires $3 \ldots 5$ bath levels. As a result, ED/DMFT can be used to investigate realistic multi-band materials. For $n_s = 9$, one iteration then takes only a few minutes. Additional details concerning the multi-band ED/DMFT approach can be found in Ref. [11].

4 Ca$_{2-x}$Sr$_x$RuO$_4$

Fig. 5 illustrates the typical modifications of the one-electron bands of Sr$_2$RuO$_4$ due to Coulomb interactions. There is an overall narrowing of bands by about a factor of two which is consistent with data obtained using angle-resolved photoemission spectroscopy (ARPES) [15]. Also, due to their finite lifetime the quasi-particle states acquire intrinsic broadening. Moreover, orbital occupancies differ from those of the bare tight-binding bands. As discussed in Ref. [9], charge is transferred from the more strongly correlated narrow $d_{xz,yz}$ bands to the wider $d_{xy}$ band, implying correlation induced enhancement of orbital polarization as a result of the planar geometry. The $d_{xy}$ van Hove singularity at M is therefore shifted very close to $E_F$. While in LDA it is about 50 meV above $E_F$ [3], correlations reduce this value to about 10 meV. Thus, the topology of the Fermi surface remains the same as predicted in LDA and confirmed in de Haas-van Alphen (dHvA) measurements. If the van Hove singularity would sink below $E_F$, the $d_{xy}$ Fermi surface would change from electron-like to hole-like, in contradiction to the dHvA data. Similar Coulomb driven internal charge redistributions are found in the systems discussed in the following sections.
The topology of the Fermi surface of Sr$_2$RuO$_4$ was controversial for several years since early photoemission data had observed the $d_{xy}$ van Hove singularity below $E_F$. This conflict was resolved when it was demonstrated [16] that the surface layer of Sr$_2$RuO$_4$ exhibits a reconstruction similar to the distortion shown in the right panel of Fig. 1. This causes a downward shift of the $d_{xy}$ band relative to the $d_{xz,yz}$ bands which is detected in surface sensitive ARPES measurements. A similar reconstruction takes place when Sr is replaced by Ca at $x = 0.5$, with the $d_{xy}$ van Hove singularity below $E_F$, as observed in ARPES [17].

As pointed out in the Introduction, Sr$_2$RuO$_4$ is metallic, but iso-electronic Ca$_2$RuO$_4$ is insulating. To understand this striking difference, it is necessary to take into account the structural distortions that occur when Sr ions are replaced by the smaller Ca ions. Similar to the surface reconstruction mentioned above, this substitution induces rotations of Oxygen octahedra, and for $x < 0.5$ also tilting and flattening of octahedra. As discussed in Ref. [18], these deformations cause hybridization among the Ru $t_{2g}$ bands, an effective narrowing of the main $d_{xy}$ component, and, most importantly, a lowering of the $d_{xy}$ band due to inter-orbital charge transfer from $d_{xz,yz}$ to $d_{xy}$. This structure induced splitting is denoted here as $\Delta = \varepsilon_{xz,yz} - \varepsilon_{xy}$. Thus, $\Delta = 0$ for the pure Sr compound ($x = 2$) and $\Delta \approx 0.4 \ldots 0.5$ eV for Ca$_2$RuO$_4$. Note that the Ca induced splitting enhances the crystal field splitting $\Delta_0 \approx 0.26$ eV present already at $x = 0$ as a result of the planar geometry [9].

Fig. 6 illustrates the enhancement of Ru $t_{2g}$ orbital polarization due to Coulomb correlations as calculated within ED/DMFT for Hund exchange $J = U/4$ and $U' = U - 2J$ [19]. $\Delta = 0$ yields only mild polarization enhancement. Thus, even at sizable Coulomb energies Sr$_2$RuO$_4$ remains metallic (see QMC/DMFT spectra in Fig. 5, left panel; ED/DMFT spectra support this conclusion). For $\Delta > 0$, however, orbital polarization increases strongly, until for $\Delta \approx 0.4 \ldots 0.5$ eV and $U \approx 3 \ldots 4$ eV, it becomes complete: $n_{xy} \rightarrow 1$ and $n_{xz,yz} \rightarrow 0.5$ (per spin), i.e., the $d_{xy}$ band is pushed below $E_F$, while the $d_{xz,yz}$ bands are half-filled. The spectra shown in the lower panels suggest that at $U \approx 3$ eV Ca$_2$RuO$_4$ is metallic, whereas at $U \approx 4.5$ eV it is insulating, with a filled $d_{xy}$ band and $d_{xz,yz}$ bands split into lower and upper Hubbard bands. Thus, because of the structural anisotropy of this layer material, Coulomb interactions modify the Ru $t_{2g}$ valence bands in qualitatively different ways.

Since the insulating phase shown in the lower right panel of Fig. 6 is paramagnetic, it corresponds to the high-temperature PI phase for $x \rightarrow 0$ in the phase diagram presented in Fig. 2. For $T < 100$ K, a (canted) anti-ferromagnetic phase is observed which has been analyzed within the LDA+U method [20].

These results show that the metal insulator transition in multi-band systems can be quite complex. Similar combinations of filling or emptying of subbands, with other subbands becoming half-filled, are found in other transition metal oxides, such as LaTiO$_3$ [21] and V$_2$O$_3$ [13, 22] which are discussed in subsequent sections. Thus, in Ca$_{2-x}$Sr$_x$RuO$_4$ there does not appear to occur a so-called orbital-selective Mott transition, as had been proposed in [20]. In the presence of narrow and wide bands, it is conceivable that these bands undergo separate Mott transitions, at different critical Coulomb energies $U_c$. As a result of correlation driven charge transfer between subbands, however, enhancement of orbital polarization appears to dominate the metal insulator transition in Ca$_{2-x}$Sr$_x$RuO$_4$. On the other hand, in the special case of half-filled particle-hole symmetric bands, orbital polarization is precluded. Narrow and wide subbands then indeed exhibit sequential, ‘orbital selective’ transitions, implying an intermediate phase in which bad-metallic behavior in the wide band coexists with insulating behavior in the narrow band [23, 24]. Depending on the nature of the Coulomb interaction between these bands, both
Fig. 6: Top panel: Correlation induced change of orbital occupancies for Ca$_{2-x}$Sr$_x$RuO$_4$ [19]. $\Delta$ denotes the splitting between $d_{xz,yz}$ and $d_{xy}$ levels due to structural distortions when Sr is replaced by Ca. Bottom panels: ED/DMFT spectral distributions for $\Delta = 0.4$ eV; solid (dashed) curves: $d_{xy}$ ($d_{xz,yz}$) components; left: metallic phase; right: insulating phase.

Transitions can be first-order, or a combination can occur of first-order transition for the narrow band and a $T = 0$ quantum phase transition for the wide band [25]. The spectral distributions shown in Fig. 6 are obtained from the interacting cluster Green’s function, Eq. (11), at real $\omega$. (For illustrative purposes, a small artificial broadening is included.) To distinguish metallic from insulating phases, the inspection of cluster spectra is sufficient. To compare with photoemission data, it would be desirable to generate the equivalent lattice spectra via Eq. (3). This can be achieved via analytical continuation of $G_m(i\omega_n) \approx G_{cl}^{el}(i\omega_n)$ or $\Sigma_m(i\omega_n) \approx \Sigma_{cl}^{el}(i\omega_n)$ to real $\omega$. The latter is preferable since one can then use $\Sigma_m(\omega)$ directly in Eq. (3), thereby avoiding the back-transformation of single-particle features stemming from $H(k)$. As discussed in Section 3, the extrapolation from Matsubara frequencies to real $\omega$ is not unique. Nevertheless, in principle, one could derive from the discrete cluster spectra shown in Fig. 6 the equivalent continuous spectra, in analogy to the non-interacting example given in Fig. 4. In the case of QMC/DMFT, real-$\omega$ spectra are usually generated via the maximum entropy method [26] which accounts for statistical uncertainties of the calculated results. In ED/DMFT inaccuracies originate from the small finite size of the bath surrounding the quantum impurity. Extrapolations of $\Sigma_m(i\omega_n)$ or $G_m(i\omega_n)$ to real $\omega$ can be done, for example, using the routine ‘ratint’ [27], as discussed in [11] for Na$_x$CoO$_2$ (see Section 8).
Fig. 7: Left: Comparison of photoemission spectra for SrVO$_3$ and CaVO$_3$ at low and high photon energies [28]. Right: QMC/DMFT spectra for SrVO$_3$ and CaVO$_3$ [29].

5 SrVO$_3$ and LaTiO$_3$

In the preceding section we have seen that Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ have fundamentally different electronic properties, even though both have four electrons in the Ru 4$d$ $t_{2g}$ valence shell. Evidently small differences of single-particle interactions due to structural distortions can lead to qualitatively different results once strong local Coulomb interactions are taken into account, with metallic (superconducting) behavior in one limit and paramagnetic or anti-ferromagnetic insulating behavior in the opposite limit.

Analogous qualitative differences exist in 3$d^1$ materials, such as SrVO$_3$ and LaTiO$_3$ [21]. The former system is a cubic perovskite. Thus all six V $t_{2g}$ spin bands are perfectly degenerate, with occupancy 1/6. Coulomb correlations do not affect this degeneracy, i.e., orbital polarization remains zero. Thus, although the on-site Coulomb energy of V ions is much larger than the single-particle band width ($U \approx 5.55$ eV, $J \approx 1.0$ eV, compared to $W \approx 2.5$ eV), the only effects that occur due to correlations are band narrowing of the quasi-particle peak near $E_F$, broadening of quasi-particle states due to finite lifetime, and satellite formation associated with lower and upper Hubbard bands [29].

Fig. 7 shows these effects for SrVO$_3$ and CaVO$_3$. The latter exhibits slight deviations from cubic symmetry due to the smaller size of Ca ions compared to Sr. The occupied part of the spectrum can be compared with the photoemission data shown in the left panel. The unoccupied range can be compared to inverse photoemission spectra. A crucial point here is to be aware of the surface sensitivity of photoemission data. As the experimental data indicate, bulk-like spectra taken at high photon energies tend to be less correlated than data at low energies which contain more surface contributions due to the shorter electronic escape depth. As discussed in [30] the local density of states at the surface of SrVO$_3$ is effectively narrowed compared to the bulk, as a result of the reduced coordination. (This band narrowing affects the $d_{xz,yz}$ bands more than the mainly intra-planar $d_{xy}$ band.) Thus, surface quasi-particle distributions calculated within QMC/DMFT [30] exhibit more pronounced narrowing of the main peak near $E_F$ and stronger Hubbard bands, in agreement with the experimental spectra shown in Fig. 7. A detailed discussion of correlation effects at SrVO$_3$ surfaces is given in [31].
In contrast to SrVO$_3$ and CaVO$_3$, LaTiO$_3$ exhibits sizable orthorhombic distortions, giving rise to substantially different $t_{2g}$ subband occupancies [21]. Fig. 8 shows the density of states components, indicating larger $a_g$ than $e'_g$ occupancy. QMC/DMFT quasi-particle spectra for this structure demonstrate that Coulomb correlations greatly enhance this orbital polarization. In fact, for $U = 5$ eV, $J = 0.7$ eV, the $e'_g$ bands are nearly empty, whereas the $a_g$ band is half-filled, with a Mott gap between lower and upper Hubbard bands. Effectively, therefore the $t_{2g}$ subband degeneracy is reduced from three to one. A similar orbital polarization is obtained for YTiO$_3$ which exhibits even stronger non-cubic distortions than LaTiO$_3$ [21].

In view of this striking enhancement of orbital polarization due to correlations it is interesting to inquire what happens when thin layers of a material such as LaTiO$_3$ are placed in artificial environments. In fact, heterostructures consisting of LaTiO$_3$ and SrTiO$_3$ layers have recently been observed to be metallic [33] although both systems in their bulk forms are insulating. (SrTiO$_3$ with 3$d^0$ is a band insulator.) The natural explanation of the observed metallicity appears to be the interface layer of Ti ions with 3$d^{0.5}$ occupancy. On the other hand, it is likely that the first few layers of LaTiO$_3$ grow in a tetragonal fashion, with the $a/b$ plane dictated by the cubic SrTiO$_3$ substrate. The lower left panel of Fig. 8 shows that the crystal field splitting of a hypothetical tetragonal LaTiO$_3$ structure has the opposite sign compared to the usual orthorhombic
version. Moreover, the band width is appreciably larger. ED/DMFT calculations then indicate that correlations enhance this reversed orbital polarization, with a Mott transition at considerably larger $U_c > 6 \text{ eV}$ within the quarter-filled doubly degenerate $d_{xz,yz}$ bands and the $d_{xy}$ band empty [32]. Although the true structure of interlayer LaTiO$_3$ has not yet been determined, these results suggest that the tetragonal compound is a strongly correlated metal rather than a Mott insulator. Thus, the observed metallicity of LaTiO$_3$/SrTiO$_3$ heterostructures should arise not only from the interface Ti $3d^{0.5}$ ions but from the entire LaTiO$_3$ layer.

6 La$_{1-x}$Sr$_x$TiO$_3$

The remarkable orbital polarization close to the Mott transition of Ca$_2$RuO$_4$ and LaTiO$_3$ discussed in Sections 4 and 5, in particular, its sensitivity to structural distortions, raises the questions: How robust are these metal insulator transitions against doping, i.e., deviations from integer occupancy? How do the different $t_{2g}$ subbands participate in the doping process? Of course, if all bands are identical as in cubic SrVO$_3$, doping affects all subbands in the same way. Fig. 9 suggests a fundamentally different picture in the case of La$_{1-x}$Sr$_x$TiO$_3$. The nearly complete orbital polarization of the Mott phase is greatly diminished, giving rise to a large flow of charge from the half-filled $a_g$ band to the empty $e'_g$ bands. For instance, at 5% hole doping ($n = 0.95$), $n_{ag} \approx 0.32$ and $n_{e'_g} \approx 0.08$ per spin band, increasing the total $e'_g$ occupancy from near zero to 0.31 and decreasing the total $a_g$ occupancy from near unity to 0.64. Thus, the internal charge flow is six times larger than the external charge transfer. Evidently external hole doping takes place via simultaneous electron and hole doping of $t_{2g}$ subbands. Analogous results are found for electron doping [34].

This behavior may be understood by analyzing the variation of the subband occupancies with chemical potential. As shown in the right panel of Fig. 9, the subband charge compressibilities $\kappa_m = \partial n_m / \partial \mu$ have opposite signs and their magnitudes are much larger than the average charge compressibility. Near the Mott transition the $\kappa_m$ become singular, permitting large internal charge rearrangements. These result indicate that the combined effect of charge and orbital degrees of freedom leads to a non-trivial generalization of the one-band picture close to half-filling and of the multi-band picture involving identical orbitals.
Fig. 10: **Left:** $V_2O_3$ $t_{2g}$ subband occupancies as functions of $U$, derived within ED/DMFT [35] for $t_{2g}$ density of states shown in Fig. 4. Blue dots: Hund exchange, solid red dots: Ising exchange; empty red dots: QMC/DMFT results for Ising exchange [13]. **Right:** blue and green curves: $a_g$ and $e'_g$ spectral distributions, red curve: total density, in the insulating phase of $V_2O_3$, calculated within QMC/DMFT [22].

7 $V_2O_3$

The transition between paramagnetic metallic and insulating phases of $V_2O_3$ observed at $T \approx 150 \ldots 400$ K [36] has been studied using DMFT by several groups [13, 22]. As in the case of SrVO$_3$, the partially occupied valence bands correspond to V $3d$ $t_{2g}$ orbitals. Because of the corundum lattice structure, these orbitals are split into singly-degenerate $a_g$ and doubly-degenerate $e'_g$ components, whose densities of states are shown in Fig. 4 [13]. Within LDA, the subband occupancies are $n_{a_g} = 0.275$ and $n_{e'_g} = 0.362$ per spin band (total occupancy $n = 2$). Fig. 10 shows that in the presence of local Coulomb interactions, this orbital polarization is amplified, until, in the range $U \approx 5.1 \ldots 5.6$ eV (for $J = 0.7$ eV), it becomes complete: The $e'_g$ bands are half-filled and the $a_g$ band is empty. As shown by the spectral distributions on the right [22], the $e'_g$ bands exhibit lower and upper Hubbard bands, while the $a_g$ band is pushed above $E_F$.

The $V_2O_3$ subband occupations as functions of $U$ reveal slight differences between full Hund exchange in the quantum impurity calculation and the more approximate Ising-like exchange. In particular, the critical $U_c$ is about 10% smaller for Ising exchange. The latter amounts to the neglect of spin-flip and pair-exchange terms in the Hamiltonians $H$ and $H^{cl}$, i.e., the last terms in Eqs. (4) and (8). Thus, only density-density Coulomb and exchange interactions are included. This approximation is usually made in QMC/DMFT calculations to avoid sign problems. In ED/DMFT these problems do not arise. Thus, both Hund and Ising-like exchange can be included. The solid and red dots in the left panel of Fig. 10 are for identical LDA density of states input and for the same Ising-like exchange, demonstrating excellent agreement between ED/DMFT [35] and QMC/DMFT [13].

The correlation driven enhancement of orbital polarization in $V_2O_3$, Ca$_2$RuO$_4$ and LaTiO$_3$ shown in Figs. 10, 6 and 8, can be illustrated schematically as indicated in Fig. 11. The occupied part of the uncorrelated density of states of these transition metal oxides has contri-
**Fig. 11**: Schematic illustration of correlation driven enhancement of orbital polarization. Upper row: crystal field split \( t_{2g} \) LDA densities of states for occupancies \( n = 1, 2, 4 \), corresponding to \( \text{LaTiO}_3 \), \( \text{V}_2\text{O}_3 \) and \( \text{Ca}_2\text{RuO}_4 \), respectively. Blue curves: singly-degenerate \( a_g \) band, red curves: doubly-degenerate \( e'_g \) bands. In the case of \( \text{Ca}_2\text{RuO}_4 \), \( a \) refers to \( d_{xy} \), \( e \) to \( d_{xz,yz} \). The vertical bars denote the Fermi level. Lower row: orbitally polarized Mott phase. \( n = 1 \) : empty \( e'_g \) bands, lower and upper Hubbard peaks of half-filled \( a_g \) band; \( n = 2 \) : empty \( a_g \) band, lower and upper Hubbard peaks of half-filled \( e'_g \) bands; \( n = 4 \) : filled \( a_g \) band, lower and upper Hubbard peaks of half-filled \( e'_g \) bands.

In the strongly correlated metallic phase, this remains true, except that orbital polarization is increased. In the insulating Mott phase, however, some sub-bands are completely empty or filled, while the remaining ones are half-filled and split into lower and upper Hubbard bands. The Mott gap therefore involves transitions between states of opposite symmetry character. Note, however, that other materials can exhibit a different behavior. The hypothetical tetragonal structure of \( \text{LaTiO}_3 \) shown in Fig. 8 reveals a Mott phase with \( n_{xz,yz} \rightarrow 1/4 \) and \( n_{xy} \rightarrow 0 \) \[32\]. Moreover, orbital polarization in \( \text{BaVS}_3 \) was shown to decrease with increasing local Coulomb interaction \[37\]. Also, the Mott transition in \( \text{LaVO}_3 \) and \( \text{YVO}_3 \) occurs before orbital polarization is complete \[38\]. Finally, in Section 4 we pointed out the possibility of orbital selective Mott transitions. Thus, 60 years after Mott first discussed the paramagnetic, correlation induced metal insulator transition, multi-band DMFT treatments reveal that these transitions in realistic transition metal oxides can be highly complex.

### 8 \( \text{Na}_{0.3}\text{CoO}_2 \)

In Section 4 we have seen that Coulomb correlations in \( \text{Sr}_2\text{RuO}_4 \) give rise to a charge transfer between \( t_{2g} \) orbitals, so that the \( d_{xy} \) van Hove singularity at the M point of the Brillouin Zone is pushed very close to the Fermi level. A slight reduction of the band width, as induced via \( \text{Sr} \rightarrow \text{Ca} \) substitution, together with moderate Coulomb interactions, shifts this singularity below \( E_F \), so that the topology of the \( d_{xy} \) Fermi surface sheet changes from electron-like to hole-like. The Fermi surface of the layer compound \( \text{Na}_x\text{CoO}_2 \) has remained controversial for several years,
Fig. 12: Upper panels: LDA $t_{2g}$ bands of Na$_{0.3}$CoO$_2$ and Fermi surface (schematic), revealing six small $e'_g$ hole pockets [39]. Lower panel: Subband occupancies as functions of $U$ for several fixed values of $J$, derived within ED/DMFT. $H_1$ and $H_2$ denote tight-binding Hamiltonians with slightly different $t_{2g}$ crystal field splittings: $\Delta_1 \approx -130$ meV, $\Delta_2 \approx -10$ meV [42].

raising the question whether Coulomb correlations might be the origin of the discrepancies between LDA predictions [39] and photoemission data [40]. As shown in Fig. 12, because of the hexagonal structure of this material, the LDA Fermi surface exhibits six small hole pockets arising from the partially filled Co $e'_g$ subbands which have not yet been observed using ARPES. Na$_x$CoO$_2$, with $3d^{5.5+x}$ occupancy of the Co $3d$ bands, as a function of Na doping reveals a remarkably rich phase diagram, ranging from Mott insulator at $x = 0$, superconductor at $x = 0.3$ (if hydrated), charge disproportionation at $x = 0.5$, pronounced Curie-Weiss behavior near $x = 0.7$, and band insulator at $x = 1$. The presence of the hole pockets is believed to have a strong influence on the nature of the superconductivity at $x = 0.3$. Thus, it is clearly important to understand the topology of the Fermi surface.

Early attempts to reproduce these measurements by taking into account strong local Coulomb interactions within the Co $3d$ shells failed since QMC/DMFT results revealed stabilization of the $e'_g$ pockets, rather than their disappearance [41]. An extensive analysis within ED/DMFT demonstrated that orbital polarization between Co $t_{2g}$ subbands may increase or decrease, depending on the details of the input single-particle Hamiltonian [42], as shown in the lower panel of Fig. 12. A crucial parameter is the $t_{2g}$ crystal field splitting, $\Delta = \varepsilon_{a_g} - \varepsilon_{e'_g}$. As long
as \( \Delta \leq -0.1 \) eV as predicted within LDA, Coulomb correlations within single-site DMFT consistently yield \( e'_g \) pockets, whereas \( \Delta > 0.1 \) eV pushes the \( e'_g \) bands sufficiently down so that the pockets disappear [43]. Thus, the fate of the \( e'_g \) pockets is more strongly influenced by single-particle effects governing the sign and magnitude of \( \Delta \) than by correlation effects. Recent quantum chemical calculations, with special focus on the strong Co 3d – O 2p covalency, yield \( \Delta \approx 0.3 \) eV [44], suggesting filled \( e'_g \) pockets. On the other hand, surface effects might also shift the \( e'_g \) bands down [45], which could explain surface sensitive ARPES data. More theoretical and experimental work is needed to clarify the Fermi surface of \( \text{Na}_{0.3}\text{CoO}_2 \).

We close this section by discussing the analytical continuation from Matsubara frequencies to the real-\( \omega \) axis. As pointed out in Section 3, quasi-particle spectra at real frequencies can be derived by transforming the solid Green’s function \( G_m(i\omega_n) \) to real \( \omega \), or by first transforming \( \Sigma_m(i\omega_n) \) and then applying Eq. (3) at real \( \omega \). The comparison shown in Fig. 13 proves that both methods are consistent, and that the latter scheme retains finer spectral details originating from the single-particle Hamiltonian. For instance, the \( e'_g \) spectrum obtained via Eq. (3) and \( \Sigma_m(\omega) \) shows two peaks below \( E_F \) which evidently are the shifted and broadened density of states features near 0.4 and 0.8 eV below the Fermi level. Also, the peak close to \( E_F \) exhibits some of the fine structure of the single-particle density of states. These details are lost if the spectrum is instead derived via extrapolation of \( G_m(i\omega_n) \) to real \( \omega \).

### 9 DMFT for Heterostructures

So far we have discussed bulk properties of strongly correlated transition metal oxides. The analysis of these properties using photoemission is nevertheless non-trivial because of surface induced changes of the electronic structure, such as band narrowing due to reduced coordination, surface crystal field splitting of \( t_{2g} \) orbitals, lateral surface reconstruction, etc. Frequently, surface contributions to photoemission spectra tend to be more correlated, with stronger Hubbard satellites than the bulk components. In addition to surfaces, heterostructures made out of
thin layers of transition metal oxides have recently attracted a lot of interest as promising candidates for electron-correlation-based devices. In Section 5, we mentioned the example of the Mott insulator LaTiO\textsubscript{3} which exhibits metallicity when it is combined in heterostructures with the band insulator SrTiO\textsubscript{3} [33].

Inhomogeneous correlated layered systems have been studied within DMFT by several groups. Here we briefly discuss a new embedding approach [46] which permits an efficient application of DMFT to semi-infinite surfaces and heterostructures. The semi-infinite substrate leads connected to both sides of the central region of interest are represented via complex, energy-dependent embedding potentials that incorporate one-electron as well as many-body effects within the substrates. As a result, the number of layers which must be treated explicitly in the layer-coupled DMFT equation is greatly reduced compared to previous schemes. The interface region is assumed to include the first few surface layers of the actual substrates. Both the central region and the substrates may exhibit strong correlation effects.

Let us consider for simplicity a simple cubic lattice with nearest neighbor hopping \( t \). The interface region has layer index \( 1 \leq i \leq N \), the left substrate \( i \leq 0 \) and the right substrate \( i \geq N + 1 \). The DMFT calculation for this heterostructure then consists of three steps: First, the self-energies \( \Sigma_{\alpha}(i\omega_n) \) of the infinite substrate bulk materials are calculated, using the formalism outlined in Sections 2 and 3. The index \( \alpha = L, R \) denotes the left or right substrate. Second, the embedding potentials for the surface layers \( i = 1 \) and \( i = N \) of the interface region are derived from the expression

\[
S_{\alpha}(k, i\omega_n) = \left( w - \sqrt{w^2 - 4t^2} \right)/2
\]

\[
w = i\omega_n + \mu - \varepsilon(k) - \Sigma_{\alpha}(i\omega_n),
\]

where \( \varepsilon(k) = -2t[\cos(k_x) + \cos(k_y)] \). The effective Hamiltonian for the interface region is given by the \( N \times N \) matrix

\[
H_{ij}(k, i\omega_n) = -t_{ij} + \delta_{ij}[\varepsilon(k) + \delta_{ij}S_L(k, i\omega_n) + \delta_{iN}S_R(k, i\omega_n)].
\]

The local lattice Green’s function and the corresponding impurity Green’s function are

\[
G_i(i\omega_n) = \sum_k [i\omega_n + \mu - H(k, i\omega_n) - \Sigma(i\omega_n)]^{-1}
\]

\[
G_{0,i}(i\omega_n) = [G_i(i\omega_n)^{-1} + \Sigma_i(i\omega_n)]^{-1},
\]

where \( H(k, i\omega_n) \) and \( \Sigma(i\omega_n) \) denote the matrices \( H_{ij}(k, i\omega_n) \) and \( \delta_{ij}\Sigma_i(i\omega_n) \). Finally, the \( G_{0,i}(i\omega_n) \) are used as input for the ED/DMFT calculations for each interface layer, providing the new self-energies \( \Sigma_i(i\omega_n) \).

Fig. 14 illustrates the layer variation of the quasi-particle weight \( Z_i \approx 1/(1 - \text{Im} \Sigma_i(i\omega_0)/\omega_0) \) for a model heterostructure consisting of a simple cubic lattice, with local Coulomb interaction \( U = 6 \) for the weakly correlated metallic substrates and \( U = 10, 12 \) for the more strongly correlated interface region \( i = 1 \ldots 4 \) (energy unit is \( t = 1 \)). The calculation is carried out using \( N = 8 \) embedded layers, which comprise the central 4-layer film and the two outermost layers of the substrates. At each layer, the impurity level is surrounded by 7 bath levels in the ED/DMFT calculation. The quasi-particle weight of the substrate surface layers, \( Z_{2,7} \), is seen to be reduced whereas at the surfaces of the poor metal it is enhanced. Evidently, the good or bad metallic character of one metal spills over into the neighboring metal [46].
Fig. 14: Left panel: Quasi-particle weight $Z_i$ of the heterostructure consisting of a 4-layer film ($i = 3 \ldots 6$) sandwiched between two semi-infinite metals, calculated using ED/DMFT [46]. Temperature $T = 0.02$. Right panel: Layer variation of spectral distribution at metal insulator interface, calculated using NRG/DMFT [47]. $x = 0$: metallic surface layer; $x \geq 1$: successive layers in insulator. Inset: low-frequency region.

Analogous layer-dependent DMFT calculations were recently performed for thick slabs using NRG as impurity solver [47]. The right panel of Fig. 14 shows the layer variation of the spectral distribution at a metal insulator interface. Metallic states near $E_F$ are seen to form exponential tails within the Mott gap of the insulator. With increasing $U$ in the insulator, the gap gets progressively wider and the penetration depth of metallic tails in the insulator decreases rapidly.

10 Cluster DMFT: Organic Salts

The influence of spatial quantum fluctuations on the nature of the Mott transition in strongly correlated systems is currently of great interest. To address this problem within DMFT it is necessary to go beyond the single-site or local approximation discussed in Sections 2 and 3 and include Coulomb interactions within clusters rather than single atoms [48, 49]. This extension allows one to study the momentum variation of the self-energy and examine, for instance, whether the Mott gap opens uniformly across the Fermi surface, or whether it appears first at the so-called ‘hot spots’ (strongly correlated points or regions of the Brillouin Zone) and only subsequently (at larger $U$) at ‘cold spots’ (weakly correlated regions).

A class of materials in which spatial fluctuations can be studied in detail are the layered charge transfer salts of the $\kappa$-(BEDT-TTF)$_2X$ family, where $X$ denotes an inorganic anion. The electronic properties of these compounds have been shown to be highly sensitive functions of hydrostatic pressure [50, 51]. As a result, the temperature versus pressure phase diagram is remarkably rich, exhibiting Fermi-liquid and bad-metallic behavior, superconductivity, as well as paramagnetic and anti-ferromagnetic insulating phases, with striking analogies to the phase diagrams of transition metal oxides obtained via chemical doping [1].

A feature of particular interest in these salts is magnetic frustration. Since their structure corresponds to an anisotropic triangular lattice, with inequivalent nearest neighbor hopping interactions $t$ and $t'$, long-range magnetic ordering becomes increasingly frustrated for $t' \rightarrow t$, giving rise to a spin-liquid phase in the absence of symmetry breaking [52]. Such a spin-
Fig. 15: Upper panels: Phase diagrams of Hubbard model for anisotropic and isotropic triangular lattices ($t' = 0.8t$ and $t' = t$, respectively), evaluated within cluster ED/DMFT for $t = 0.04\, \text{eV}$ [53]. Plotted are the first-order metal-insulator phase boundaries as functions of inverse local Coulomb energy $U$. In the experimental setup increasing hydrostatic pressure $P$ implies increasing band width $W$ or decreasing $U$. Lower panels: Temperature / pressure phase diagrams for organic salts, $\kappa$-Cl [50] (left) and $\kappa$-CN [51] (right). The reentrant behavior observed for $\kappa$-Cl is absent for $\kappa$-CN.

The minimal model Hamiltonian that captures the interplay between geometrical frustration and strong Coulomb interaction present in the conducting layers of organic salts is

$$H = -\sum_{ij\sigma} t_{ij}(c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma}, \quad (20)$$

where the sum in the first term is limited to nearest neighbor sites. The hopping integrals in a unit cell consisting of three sites are $t_{13} = t_{23} = t$ and $t_{12} = t'$. The chemical potential $\mu$ is fixed at half-filling. Within cluster DMFT the lattice Green’s function is defined as

$$G_{ij}(i\omega_n) = \sum_k [i\omega_n + \mu - t(k) - \Sigma(i\omega_n)]^{-1}_{ij}, \quad (21)$$
where $\mathbf{k}$ extends over the reduced Brillouin Zone. $t(\mathbf{k})$ denotes the hopping matrix for the superlattice and $\Sigma(i\omega_n)$ represents the non-diagonal cluster self-energy matrix.

Fig. 15 shows the ED/DMFT phase diagrams for the anisotropic and isotropic triangular lattices. The critical temperatures, $T_c \approx 50$ K are consistent with the measured values for $\kappa$-Cl and $\kappa$-CN. For $t' = 0.8t$, the phase boundaries separating the Fermi liquid from the Mott insulator show the same kind of reentrant behavior as measured for $\kappa$-Cl. For instance, at $U = 1/3$ eV and $T \approx 50$ K the system is a Mott insulator which turns into a Fermi liquid when $T$ is lowered to about 20 K. Further reduction of $T$ reverts the system to a Mott insulator, just as seen in the data. This reentrant behavior is absent in the case of the isotropic triangular lattice. This striking difference can be understood by analyzing the magnetic correlations $<S_{iz}S_{jz}>$ shown in Fig. 16. The results demonstrate that spin correlations are strongly enhanced as the geometrical frustration is suppressed. Thus, $t' = 0.8t$ induces a stronger tendency towards magnetic order than $t' = t$. At low $T$, therefore, the electron entropy is suppressed for $t' = 0.8t$ as compared to $t' = t$. As $T$ is increased for $t' = 0.8t$, the system lowers its free energy by transforming to a metal since the entropy of the metal exceeds that of the ordered insulator. At even higher temperatures the system gains entropy of $\log(2)$ by transforming back into a paramagnetic insulator. In the isotropic lattice magnetic ordering is suppressed and the reentrant behavior disappears.

Finally, to illustrate the first-order nature of the metal-insulator transition we show in the right panel of Fig. 16 the spectral weights at $E_F = 0$ for the three cluster sites as functions of $U$. These quantities exhibit hysteresis for increasing and decreasing $U$, indicating coexistence of metallic and insulating solutions.
11 Summary

DMFT provides a combination of (i) high-quality single-electron Hamiltonians for complex materials consisting of many electrons per unit cell and (ii) accurate many-body formalisms for the study of complex quantum impurities. Together with increasingly powerful computational resources, this combination today allows detailed studies of the electronic properties of strongly correlated systems, such as transition metal oxides and organic salts. As a result, the nature of the Mott transition in multi-orbital compounds and its remarkable sensitivity to key parameters, like doping, temperature, pressure, crystal symmetry, etc., are now much better understood than only a decade ago.

The examples discussed in this lecture demonstrate that finite temperature exact diagonalization has emerged as a versatile and efficient tool for the study of highly correlated materials. The correlation induced charge transfer between valence orbitals is now a well established phenomenon found in a variety of systems. In the future, it should become feasible, via generalizations of DMFT for inhomogeneous systems, to investigate these kinds of effects at neutral and charged heterostructures consisting of realistic transition metal oxides. Further studies of spatial fluctuations, by combining exact diagonalization with cluster DMFT, will also be of great interest.

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